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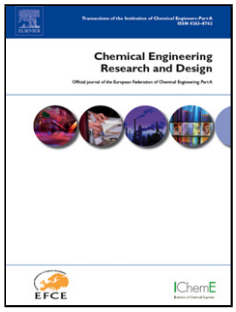

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Spinach-based photo-catalyst for selective plating on polyimide-based substrates for micro-patterning circuitry

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Graphical abstract

Highlights

- For the first time copper microtracks are photo-catalysed by a plant extract
- Spinach extract is used as a catalyser for the synthesis of Ag NPs on polyimides
- The photo-patterning reaction is accelerated by an order of magnitude
- Highly conductive, photo-induced selective electroless copper plating is obtained
- A simple extraction method of chlorophyll-A from spinach at 120 mg/L is developed

Abstract

This work demonstrates the suitability of spinach extract as a bio-catalyser for the photo-catalysed synthesis of silver nanoparticles on polyimide and polyetherimide, and their suitability as a seed-layer for the formation of conductive micro-track after plating. The study reveals that the extract can accelerate the reaction rates of the photo-patterning process by an order of magnitude, when applied on materials for flexible electronics and 3D printing. The two main components of the extract that can act as photo-catalysers - chlorophylls and plasmatic salts - have been individually studied by energy-dispersive X-rays, UV/VIS spectroscopy and X-ray Diffraction. A simple and well-defined method for extraction of chlorophyll-A (Ch-A) from fresh spinach at 120 ± 20 mg/L, has been developed. The study reveals that the main component enhancing photoreduction rates is due to the ionic salts present in the extract. The spinach extract has been demonstrated to be a valid catalyser to achieve highly conductive, selective electroless copper plating of track features, of thickness 0.5 ± 0.2 µm and conductivity (0.7 ± 0.2) $\times 10^7$ S/m. 10 µm wide tracks are obtained, and the copper plating withstands the adhesion test. Demonstration of selective, ionic-liquid immersion plating of silver onto electroless copper, highlights a high quality metal protective layer finishing process desirable for reduced waste and toxicity.

Keywords: chlorophyll, silver nanoparticles, selective plating, photo-patterning, flexible electronics, polyimides

1 Introduction

The global consumer electronics market has a predicted compound annual growth of 4 % by 2022, with a value of US $1,55Tn[1]. The outcome of this mass production is the generation of waste chemical solutions resulting from electrochemical industries such as those involved in metal finishing, printed circuit board, semiconductor devices and wafer manufacture. High restrictions and environmental regulations are imposed on how chemicals are disposed safely, incurring high costs for manufacturing companies[2]. The substitution of toxic chemistry with more environmentally friendly chemicals is highly desirable for a) the reduction of storage and disposal costs of waste chemistry; b) improved work health and safety; and c) a reduction to environmental footprint of manufacturing industries. Replacing

these chemicals with economic and environmentally friendly alternatives, which also provide no reduction to manufacturing quality is a highly desirable processing challenge that is supported by international government policies.

In conventional lithographic-based electronic circuitry manufacture, a large volume of copper (Cu) waste is incurred due to the subtractive nature of the manufacturing procedure, where a large percentage of the total Cu surface is etched away. Direct Metallisation (DM) processes offer a lower material wastage whereby metallic features are directly patterned onto a substrate, therefore removing the need for lithographic metallic etching[3]. A suitable seed layer for DM can be obtained optically[4, 5], chemically[6], thermally[7] or by high energy radiation[8, 9]. Of particular interest is visible light, optically induced reduction of silver (Ag) metal nanoparticles due to its fast processing speed and low thermal output - resulting in low damage to substrate surface relative to other optical reduction wavelengths[10]. Photoreduction presents some challenges, and from a large list of metallic ions used in electronics, silver is one of the most suitable ones for this[11]. Highlighted in Figure 1 is a Ag-based DM technique using optical reduction applying first, hydrolysis of a high-temperature polyimide-based plastic and ion exchange of Ag ions into its hydrolysed surface. Next, the surface is sensitized with a photo-catalyser agent, which is critical for accelerating the reaction and obtaining a process of industrial interest[4]. This is followed by a selective photoreduction of the Ag ions to Ag metal using visible light (460 nm) and an optical mask. At this stage, the ions in the masked regions which have not been photo-reduced are chemically removed, resulting in a substrate with only the reduced Ag metal on the surface which acts as a catalytic seed layer for electroless copper (Cu) plating. Using this technique high quality conductive micro-tracks[4] can be written onto polymer surfaces for use in electronic device manufacture. The technique also yields itself to the patterning of 3-D geometries for the development of new and innovative shapes as structural electronics[4]. Optical sensitisation enables increased photoreduction rates and contributes to the DM process outlined in Figure 1.

Other materials can help further reducing the environmental footprint, namely the use of plant extracts and ionic liquids.

Plant extracts have shown potential as reducing agent for graphene[12] and metal nanoparticle green synthesis[13], mainly in suspensions[14], and a variety of methods have been developed using plants such as Amaranthus Gangeticus[15], Bridelia retusa fruit[16], or

Buddleja globosa[17]. To the best of the authors' knowledge, no work has been performed to date applying plant extracts in the DM of microelectronics circuitry. Spinach-extract has been shown as reducing agent for silver NP synthesis in solution[18] and recently we have demonstrated its use as optical sensitiser[19] on polymer. Its use provides a renewable, low toxicity, 'green chemical' alternative to traditional optical sensitisers[20]. It is also a crop used in food production and so does not contribute to the issue of dedicated crop in the renewable energy debate[21]. Spinach-sourced components have also been shown to be useful for the synthesis of bioplastics[22] and as light harvesters[23].

Ionic Liquids (IL) are a relatively new range of chemicals used in electrochemical manufacturing[24]. They require no water in their formulation which enables a manufacturer to reduce waste water environmental impact and avoid water treatment costs. IL can be used as alternatives to existing chemical solutions used in microelectronics manufacture such as immersion, electroless and electroplating[25]. A metal is deposited onto another metal to protect it from oxidation in a process referred to as metal finishing and is a requirement for Printed Circuit Board manufacture for further processing by the soldering of components[26]. IL have been formulated for metal finishing onto Cu microcircuitry, providing a low environmental foot print alternative to traditional processing such as immersion Ag plating[27].

The cost savings introduced by DM and IL, along with the introduction of an environmentally friendly optical-sensitizer chemistry, is a highly desirable collection of manufacturing processes and materials. For this reason studies were performed to characterise the performance of spinach extract for its use in electronics DM manufacture, to identify the chemicals responsible for the enhancements to process performance and to introduce a DM method for metal finishing using IL. The composition of the spinach extract was compared against other chlorophyll-based chemicals which have light harvesting properties useful for photochemical reactions[28]. The quality of the plated conductive features is also characterised to highlight the IL and sensitizer processing performance against standard microelectronic quality metrics.

2 Experimental

Experiments were performed on Polyimide-based polymers, Polyimide (PI) 25 µm Kapton® sheet from DuPont™, UK, and 75 µm thick Polyetherimide (PEI) 1000B ULTEM®, from

Cadillac Plastics Ltd., UK. Additionally, PEI filaments for Fused Deposition Modelling (ULTEM ® 9085) were purchased from Stratasys Ltd., US. Chlorophyll samples derived from spinach extract were purchased from Sigma-Aldrich UK (Merck™) and were formulated to specific concentrations. These were: Chlorophyll-A (Ch-A) ($C_{55}H_{72}MgN_4O_5$, Ch-A content 100 %), to 500 mg/L and Chlorophyll-B (Ch-B) ($C_{55}H_{70}MgN_4O_6$, Ch-B content ≥ 90 % and Ch-A ≤ 0.5 %), to 1000 mg/L. All other chemicals used were obtained from Fisher Scientific, UK. A spinach extract was made by blending into 150 mL of ethanol 50 g of spinach leaves (stalks removed) obtained from supermarket Tesco™, UK. The resulting liquid was filtered several times with grade 1 filter (1:11 μm). The spinach was divided into two samples, one kept at 4 ^{o}C in a fridge for 5 days before being used referred to here after as 'fresh sample' and the other kept at room temperature for 5 days, referred to as 'degraded sample'. Lastly, a sensitiser 0.01 M KCl was made up in 3:1, ethanol:DI water for comparison with existing DM processes[4].

The polyimide-based substrates were first cleaned with isopropanol and then hydrolysed in a heated potassium hydroxide (KOH) solution. PI and PEI were hydrolysed for 15 min at 50 ^{o}C in 1 M and 15 M KOH, respectively. After rinsing in DI water and ultrasound agitation, samples were submerged in a 0.1 M Ag nitrate ($AgNO_3$) solution for 10 minutes for ion exchange of Ag^+ onto the surface and rinsed with DI water. Photosensitization was performed by immersing the samples in the respective sensitiser solution for 30 seconds at room temperature and left to dry after. Selective photopatterning, photoreduction was achieved using an optical chrome glass mask, supplied by JD Photo-data Ltd, UK and a high power (1 W, 460 nm) LED for 30 sec duration unless stated otherwise.

Selective electroless Cu plating was performed on the Ag photoreduced surfaces using the process outlined in a previous publication[29]. This formulation allows selective plating only on the areas that present metallic seeds[30, 31]. IL immersion Ag plating was then performed on the selective electroless Cu plated surface. The IL immersion solution used comprised of 0.01 M silver nitrate and ethaline (1 ChCl:2 ethylene glycol), which was made-up to conditions outlined in[27]. The Cu plated samples we Ag IL plated at room temperature for 10 min and after, rinsed in ethanol, DI water and isopropanol.

Scanning Electron Microscope (SEM) images were obtained using a Quanta 3-D FEG and Energy dispersive X-ray (EDX) were obtained using an Oxford Instruments X-maxN 150 mm EDX detector, of photoreduced Ag on PEI and dried, fresh undiluted spinach leaf extract on silicon (Si) wafer. To evaluate the water content of the fresh undiluted spinach sample, 1

mL of solution was weighed before and after evaporation of the liquid, and the concentration of the KCl constituents derived from the average EDX % values. X-ray Diffraction (XRD) measurements were obtained with a D8 Discover, from Bruker Corporation (λ = 0.15418 nm) of photoreduced Ag on PEI, processed using fresh, undiluted spinach extract.

To evaluate the conductivity of the electroless and immersion deposits, measurement results of thickness were obtained using a Bruker Dektak 3 Profilometer. Ten measurements of the electrical resistance of the deposited metal were obtained using a two-point probe, Signatone^{TM} probe station and the average converted to conductivity using an average deposit thickness. High resolution optical images were obtained of the surfaces using a Leica DM5000 microscope. Optical absorbance spectroscopy was measured using a Perkin-Elmer LAMBDA 950 UV–Vis Spectrophotometer, for Ag photoreduced PEI surface; chlorophyll solutions A and B diluted to, 19 mL/L and 38 ml/L, respectively in ethanol; and spinach-extract solutions both in a 2:25 dilution in ethanol, poured into 10 mm optical-path cuvettes. Base line measurements for the Ag photoreduced PEI surface were obtained with blank PEI, while pure ethanol in a 10 mm cuvette was used as baseline for the solutions.

3 Results and Discussion

3.1 Photoreduction on different polyimide-based substrates

Table 1 presents high resolution images of polyimide-based materials after Ag photoreduction with optical sensitization by spinach extract and without. After photoreduction track features of 3 mm pitch were patterned on the surfaces. The degree of photoreduction is highlighted qualitatively by the change in colour of the patterned surface. A plastic thin film containing small Ag nanoparticles appears yellow due to the localised surface plasmon resonance (LSPR) of small Ag NPs[32]. If the NPs increase in size, the LSPR peak will broaden and the sample will turn reddish[33]. If the NPs grow further, they will create larger Ag aggregates with a metallic appearance[4]. Applying the spinach extract enables an increase in the degree of photoreduction, shown by an increase in the intensity and contrast of the photoreduced features and a change in colour towards darker shades. This change is likely due to a higher density of Ag metal reduced onto the surface induced by the faster photoreduction rates brought on by the spinach treatment[4].

The PI material in Table 1 displays the smallest change in response to photoreduction relative to the PEI samples. This is likely due to a smaller ion exchange of Ag ions into the PI surface. Hydrolysis of PI generates polyamic acid[34] which can be easily be removed off its surface during rinsing due to its low adhesion to PI[35], reducing therefore the amount of Ag ion exchanged and the lower, more sparse photoreduction. Regardless, the application of spinach enhances photoreduction rate on PI.

The silver-loaded PEI ULTEM 9085 filament for FDM 3D printing was successfully photo-patterned with Ag metal producing an orange-like appearance. With the application of the spinach extract a darker deposit was formed indicating a denser photoreduction. The successful patterning of PEI filament using spinach extract, highlights its application for the additive manufacturing of unique 3-D circuitry in space-saving circuit designs, which are highly desirable for satellite and automotive manufacture[36].

For the PEI flexible substrate ULTEM 1000B, two different photoreduction exposure durations were applied, 10 min and 30 sec. Increasing the exposure duration increases the degree of Ag ions photoreduced as indicated by the larger area coverage and the higher intensity of the pattern. The 10 min exposed sample reveals that, without the extract, a dark red central regions is observed where the light intensity has been higher, surrounded by extended yellow patterns. With spinach leaf extract, metallic grey features are observed with a yellow feature - bottom left of image – where the light intensity has been higher. The change in appearance observed indicates the degree of Ag metal reduction. The different colours observed for all of the photopatterned samples could be explained to the different Ag deposit density and morphology[37]. At prolonged exposures thermal reduction by heat generated from the LED beam could also contribute to the total reduction of the Ag ions[7].

The material PEI ULTEM 1000B displays the fastest photoreduction requiring the lowest LED dose (30 sec) for observable photoreduction. As such, it is more ideally suited to manufacturing which seeks to minimise chemical use and obtain a fast processing duration. For these reasons, this material has been used for the remaining investigations. From Table 1 it is possible to see that an exposure of 30 s by using the spinach extract patterns a larger area than a 10 min exposure without the extract. The energy dose difference is a factor of 20.

Figure 2 shows PEI ULTEM 1000B after selective photoreduction using fresh spinach extract. In Figure 2.A, the photoreduced region can be identified by the yellow/green patterning and the unexposed PEI by the blue/grey colour. Scratches on surface are due to

handling. SEM insert highlights nanoparticles formed on surface in response to photoreduction.

In Figure 2.B, analysis by XRD reveals the presence of a peak at 28.2° which coincides with cubic AgCl peak (111) (ICSD No. 64734). Another AgCl peak for (200) exists around 32° (ICSD No. 64734), although its low intensity barely surpasses the noise threshold[38]. No Ag metal peaks were witnessed which could be due either to the low NP density, unable to reach the noise threshold of the PEI substrate, or to an amorphous morphology of the photoreduced Ag which could broaden its peaks[39]. In Figure 2.C, UV/VIS absorbance reveals the presence of a peak around 430 nm which corresponds to reported values for Ag NP[4]. A scan of blank PEI was also provided for reference revealing no peaks. The addition of the spinach leaf extract enables photoreduction of the Ag ion, leading to the formation of Ag. The presence of AgCl peaks indicates that a constituent of the spinach extract contains Cl which has contributed to the metal salt formation. AgCl is optically sensitive to the LED wavelength applied[4] and so could contribute to the enhanced photoreduction rates witnessed.

3.2 Selective plating onto PEI ULTEM 1000B using spinach extract and ionic liquids

The photoreduced features act as catalytic sites for electroless Cu plating to form conductive electrical track features[40]. Without the spinach leaf extract electroless plating onto PEI ULTEM 1000B is unsuccessful using the conditions applied, due to the smaller amount of photoreduced Ag (samples not shown). However, selective Cu plating was achieved with the sensitised samples. Selectivity was obtained by the application of a cleaning process after photoreduction, where unreduced ions are removed off the substrate surface leaving behind reduced Ag onto which electroless plating can be performed, see Figure 1[4]. Figure 3A shows images of selective electroless Cu plating of features of size 50 to 160 µm, on PEI substrate ULTEM 1000B. The Cu deposit thickness is 0.5 ± 0.2 µm and a conductivity measured as (0.7 ± 0.2) $\times 10^7$ s/m, which is approximately one tenth the value of bulk copper (5.9 $\times 10^7$ s/m) and is equivalent to values expected for this thickness[41]. Thicker electroless Cu deposits will produce larger conductivities although at the expense of longer processing

durations and a compromise of feature selectivity[41]. Spinach residues can also be observed on the PEI surface, highlighted by irregular green spots which are present after DI rinsing of the substrate. The spinach extract was prepared by sieving with a 11 µm sized pore filter and as the contaminations have a the size of 50 µm, it is clear that they are produced from agglomeration of smaller residues in suspension.

A selectively electroless Cu plated sample was then IL immersion plated with Ag to obtain a finishing plating, which is commonly sought in the PCB manufacturing industry (Figure 3B). The Ag deposit selectively formed onto the regions where the electroless Cu had been deposited. A measure of thickness for the Ag/Cu deposit was approximately 0.9 ± 0.2 µm. Immersion plated Ag is typically of 0.1 µm thickness[26] which is below the thickness variation measured for the sample making it difficult to approximate the Ag thickness on the Cu. A measure of Ag/Cu conductivity is (0.005 ± 0.002) $\times 10^7$ s/m which is less than the Cu deposit by itself. The reason for this lower conductivity could relate to the tarnish of Ag, as Ag is susceptible to aerobic oxidation[27] and this Ag oxide/sulphide layer lowers the measured conductivity of the deposit[42]. This oxidation results in the sought protective finishing layer, which is stable and soluble in common solder compositions. Figure 3.c shows the results of the EDX analysis, revealing that copper atoms represent 14.6% of the atomic percentage, and silver atoms 7.1%. The remaining percentages are supposed to come mainly from the polymer (carbon: 65.6%; oxygen: 12.7%). These percentages reveal a ratio C:O of 5.2:1, while pure PEI presents a ratio of 6.2:1. This excess of oxygen reinforces the hypothesis of the possible partial oxidation of the silver. The SEM insert shows the silver surface, composed of small crystallites.

In order to study the resolution of the process when using the spinach extract, masks of parallel tracks with 40 and 20 µm pitch have been used. Figure 4.A presents the photopatterned tracks directly after exposure. The electroless plating does not seem to worsen the resolution, and copper tracks of 10 and 20 µm have been successfully produced (Fig.4.B and C, respectively). The adhesion of the copper has also been tested by using the Scotch tape test applied to the electroless plated samples. A representative sample is shown in Figure 4.D. After the test, the sample presents exactly the same aspect as before (Fig.4.E). An image of the tape reveals that no copper has been removed during the test (Fig.4.F), which is indicative of a good adhesion.

3.3 Spinach extract composition

The spinach extract has been analysed in order to identify the chemical responsible for photo-catalysis. Figure5 shows a SEM image of fresh undiluted spinach extract dried on a Si wafer surface revealing dendritic and cubic crystalline structures. An EDX scan indicates that carbon (C) and oxygen (O) constitute more than half of the sample and also reveals a high percentage of Si, due to it being the substrate on which the extract was analysed. Other elements such as sodium (Na), aluminium (Al), chloride (Cl) and potassium (K) are also present in lower amounts. The cubic crystals comprise of a large fraction of the extract and an EDX of them reveals that they are likely KCl due to their high elemental % instead of Na - which also forms cubic structures[43]. The extract has 7.5 g/L of dry residues. The initial mass of the spinach (water content: 91%) and the amount of ethanol used allow us to deduce that the final solution is composed of 3:1 of ethanol:water. The KCl, which is the most abundant salt in the spinach plasma, is concentrated as 0.01 ± 0.003 M in the resulting spinach extract, as derived by the mass of solute remaining after evaporation, and approximated from the average percentage as observed by EDX.

Chlorophylls have been identified as a candidate for influencing the photosensitising properties of the spinach extract due to their importance in photosynthesis[19, 28]. Using UV/VIS absorbance measurements, the composition of two diluted chlorophyll solutions A and B is compared with two 2:25 diluted spinach extracted solutions, fresh and degraded, which have been aged for five days under temperatures 4^{o}C and 25^{o}C, respectively, as shown in Figure 6. In the plot the chlorophyll samples A and B are identified from their absorption spectra with three absorption peaks at 419 nm, 615 nm and 660 nm for Chl-A and two peaks at 458 nm and 638 nm for Chl-B, which coincide with values found in the literature[44]. The absorbance spectrum of diluted fresh spinach extract shows three peaks which coincide with Ch-A spectrum, although the 419 nm also coincides with the element lutein that exists within spinach, hiding the absorption value for the chlorophyll peak[45]. The intensity of the two peaks at 615 nm and 660 nm in the diluted fresh spinach, represent an average 51 ± 9 % of the respective intensities of Ch-A peaks. From the Beer-Lambert law it can be deduced that the concentration of Ch-A in the fresh spinach extract is approximately half the value of Ch-A sample[46]. As such, the diluted sample of fresh spinach extract has approximately 10 ± 2

mg/L of Ch-A and hence, the original undiluted fresh extract is 120 ± 20 mg/L. For the 2:25 diluted degraded sample, the average of the two peaks in Ch-A, have decreased to 25 ± 9 %, which indicates that the Ch-A content in the degraded spinach extract has also decreased by the same amount, to give a Ch-A value in the diluted solution of 5 ± 1.5 mg/L, which in the undiluted solution equates to 59 ± 20 mg/L. The reduction in chlorophyll content at room temperature of approximately 60 mg/L, is related to catabolism of the chlorophyll molecules which is faster at higher temperatures[47]. The presence of Ch-B in the fresh and degraded spinach extracts is more difficult to evaluate, because the two peaks at 638 nm and 458 nm, cannot be directly identified in the spinach extract spectra. This is due to the presence of the lutein peaks in the range 420 – 470 nm which hides the Chl-B and Chl-A peaks[45, 48] and possibly due to drift of the spectrum due to the addition of ethanol in its makeup[44].

Images of the samples in curvets under UV/VIS analysis are included as inserts in Figure 6. The visible transparency differs in the solutions. Ch-A shows a turquoise-green colour whilst Ch-B is olive-green. The absorbance spectra of Ch-B is approximately double that of Chl-A, which corresponds to the concentration differences of 38 mg/L and 19 mg/L, respectively. As such, the darker appearance of the Chlorophyll solutions coincides with a greater concentration. Additionally, the visible appearance of Chl-B is more reddish that Chl-A giving it darker completion[48]. The degraded, diluted spinach solution shows the lightest shade of all the solutions, which coincides with its smaller absorption spectrum and lowest Chl-A concentration.

3.4 Photoreduction with various optical sensitiser solutions

Table 2 shows images of PEI ULTEM 1000B after photoreduction for different optical sensitiser solutions and different optical exposure durations. Photoreduction appears on all samples. Using diluted solution of Ch-A and Chlorophyll B, the photoreduction appears with the same intensity as without any sensitizer. From this it can be determined that chlorophyll does not catalyse the photoreduction reaction. The samples also show green discolouration due to staining by the high concentrations of chlorophyll.

Samples treated with fresh and degraded spinach extract reveal a rapid photoreduction with exposures of 3 s and 30 s showing an intense photopatterning that covers an area larger than

the 30 s untreated PEI. For 30 s exposure the photopatterning appears with a greater intensity for the degraded spinach extract rather than the fresh extract. The degraded extract contains less chlorophyll remaining in its composition after five days at room temperature, as shown in the previous section and yet photopatterning occurs rapidly. This could be due to un-degraded pigments in the darker, fresh chlorophyll solution, absorbing the incoming light and hindering the rate of photoreduction[49]. Finally, samples were photoreduced using a 0.01 M KCl solution and showed a similar result to the spinach extracted results, although with a lower photoreduced intensity. This is a clear indication that the sensitization by spinach extract is due to KCl content in the spinach leaf and not the chlorophylls.

In order to quantify the velocity of the photopatterning effect, different samples were prepared with the spinach extract and without it, and irradiated at different exposure times. Their absorbance was measured and is represented in Figure 7. The results show that the optical density of the samples treated with the extract increase much faster than without it. Additionally, the plasmon resonance is also broader when using the spinach extract. This can be attributed to the silver nanoparticles being synthesized on the AgCl, where they are known to present a reddish colour. Without the extract, the patterning is only visible to the naked eye for exposures longer than 30 seconds. In contrast, when using the extract, even one-second exposure is enough to reveal some patterns, which is indicative to an enhancement factor of one order of magnitude. For a more accurate calculation, the optical absorbance has been measured at 450 nm for each sample and plotted in the insert of Figure 7. The slopes of the trendlines indicate that the absorbance when using the extract escalates eight times faster than without extract (slope 0.0023 s^{-1} versus 0.0003 s^{-1}).

4 Conclusions

This study demonstrates successful micro-photopatterning on a range of polyimide-based materials and types of surfaces (planar, contoured) using low toxicity, renewably sourced, spinach-extracted photosensitiser chemistry. A simple method for preparing spinach extract with a high amount of Chl-A (120mg/L) has been used. The spinach extract assists the synthesis of Ag nanoparticles by increasing the photoreduction rate. The compound responsible for enhanced photoreduction rates was identified as the plasmatic salts within

the spinach, specifically the presence of chlorine, rather than the chlorophyll content which had no noticeable effect, even when applying chlorophyll A and B at high concentrations. Highly conductive electroless plated deposits were selectively formed on the photopatterned substrates, highlighting microelectronic fabrication applications contending to standard processes applied in industry. The application of an IL Ag finish was demonstrated on the Cu patterned surfaces highlighting the successful application of a low toxicity finish chemistry.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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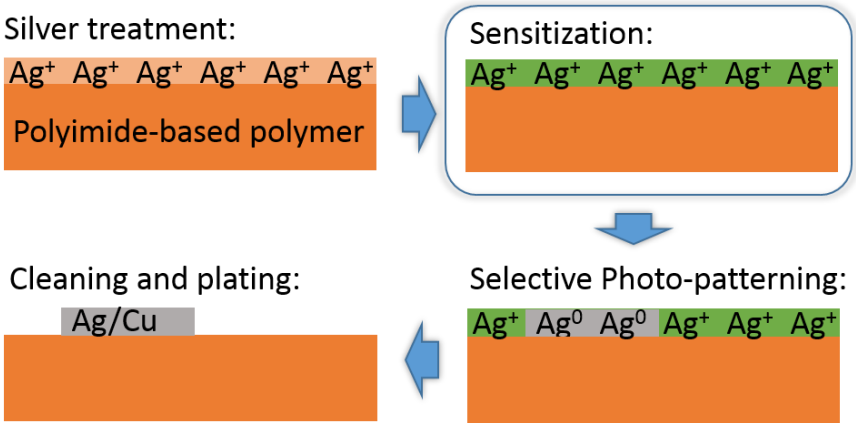


Figure 1 - Process to achieve the metallisation of polyimide-based polymers, including hydrolysis breaking of the imide ring and ion exchange of Ag and sensitization step crucial to achieve rapid photoreduction, where potassium ion is exchanged by Ag producing Ag polyamate.

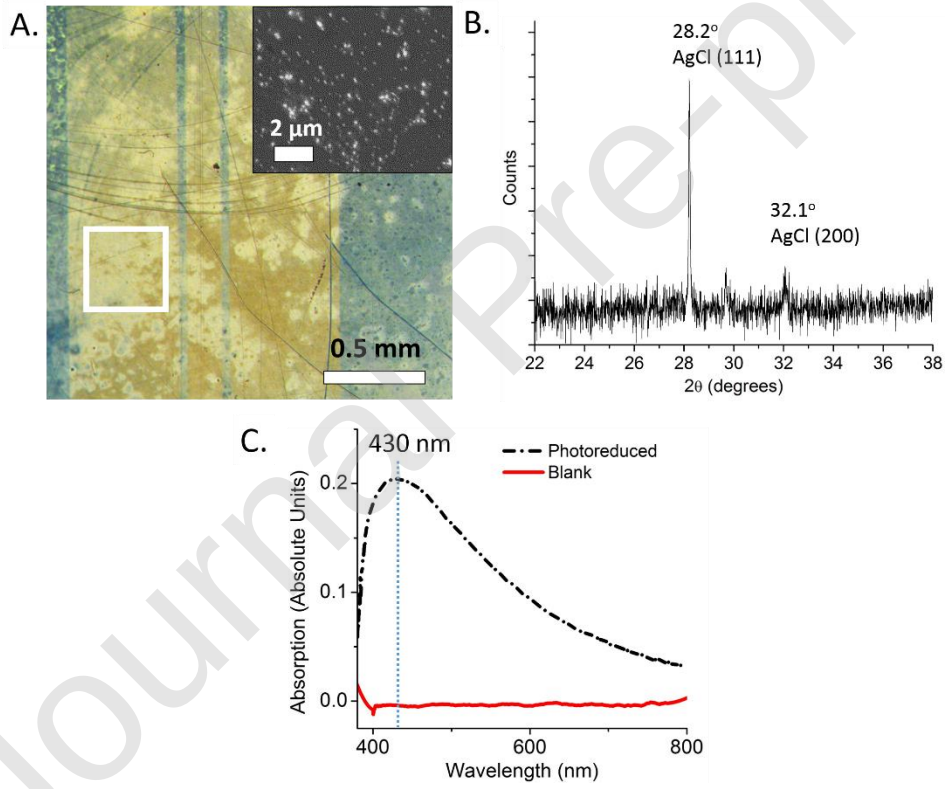


Figure 2 – PEI ULTEM 1000B after selective Ag photoreduction using fresh spinach extract showing, A) image of surface with SEM insert, B) XRD and C) UV/Vis.

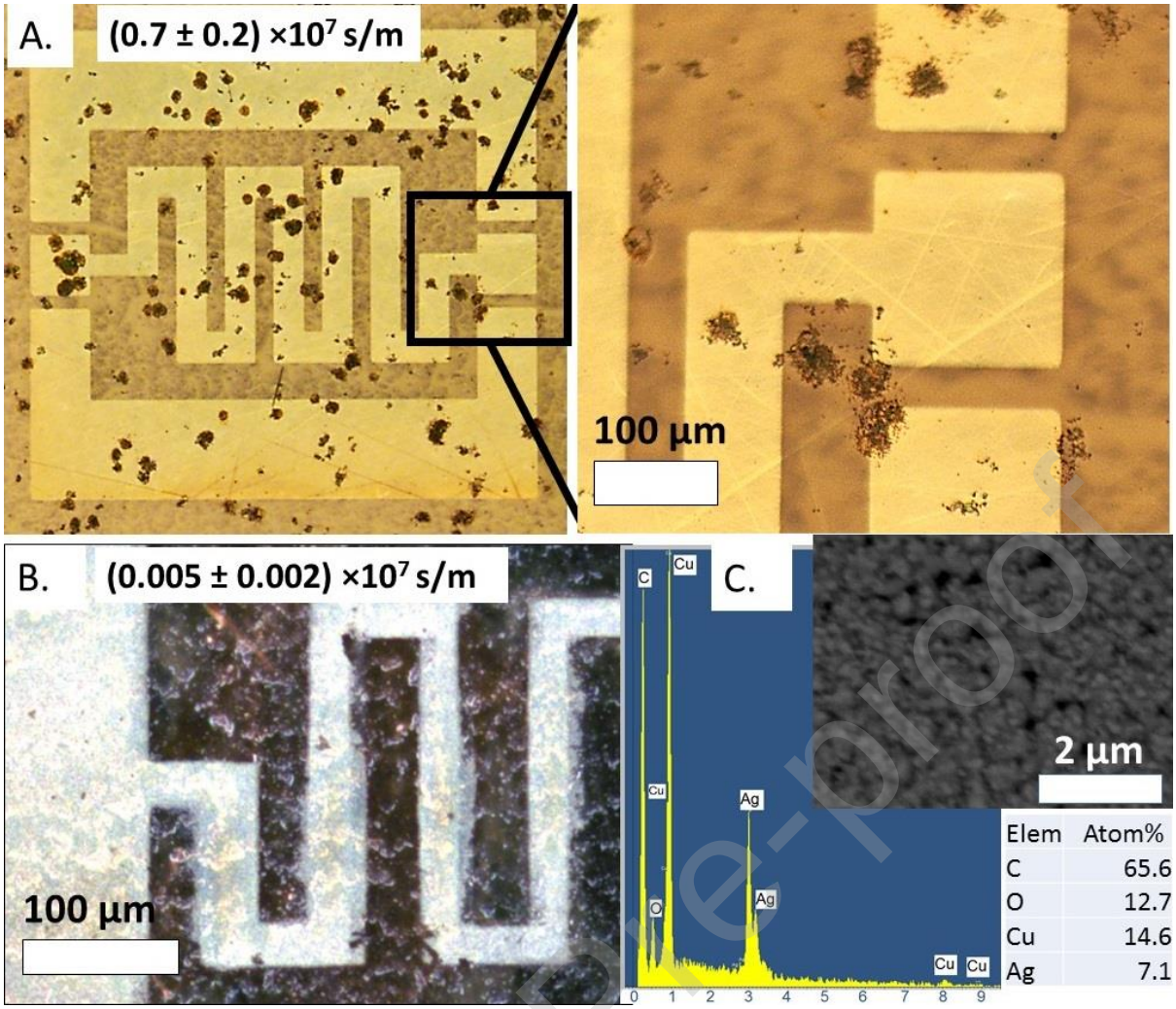


Figure 3 – A) Electroless copper plated PEI ULTEM 1000B after fresh undiluted spinach extract treatment and photopatterning. B) Ionic Liquid immersion silver plated finish on spinach-assisted electroless copper. C) EDX analysis of the final copper and silver plated sample. Insert: SEM of the surface.

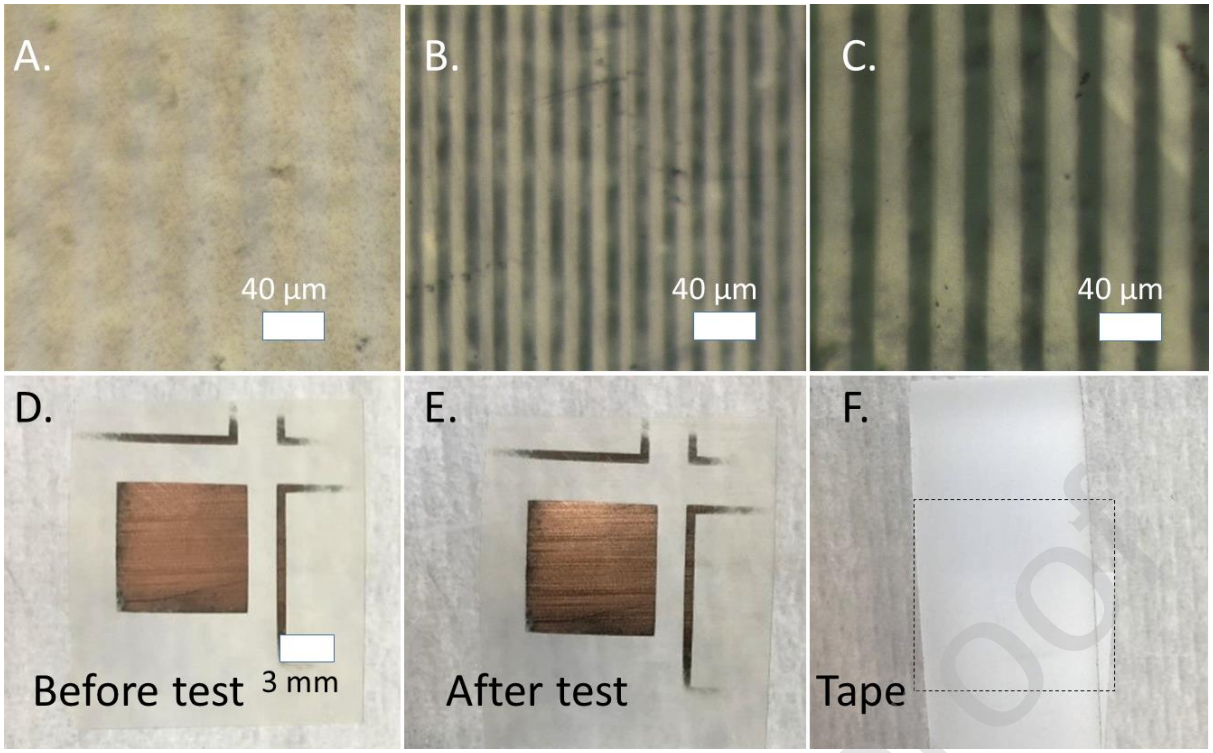


Figure 4 – A) PEI ULTEM 1000B by using spinach extract treatment and photopatterning, revealing 20 µm wide tracks. B) Patterned and electroless copper plated sample with 10 µm wide tracks, and 20 µm (C). D) Electroless copper plated sample before the tape test, and after (E). F) Image of the tape revealing that no copper has been removed.

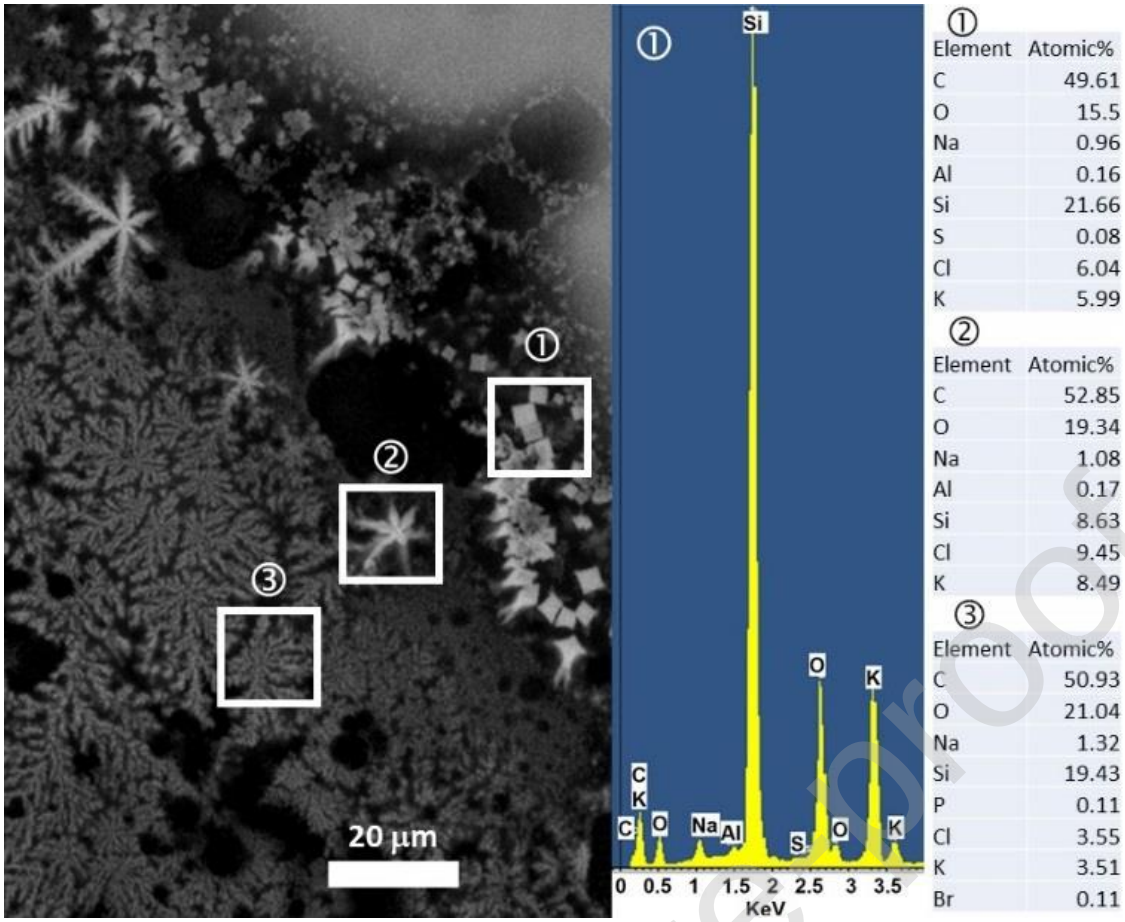


Figure 5 - SEM micrograph of dried fresh undiluted spinach extract on silicon and EDX showing the % composition of the different regions of the dried sample.

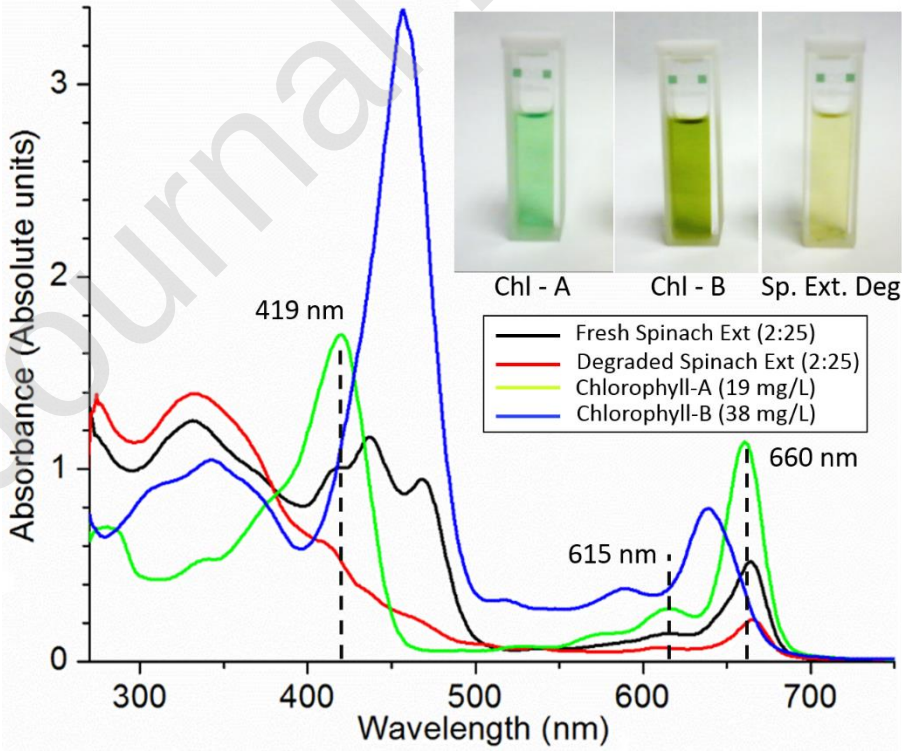


Figure 6 – UV/VIS absorbance of chlorophyll solutions Chlorophyll-A and Chlorophyll-B, and 2:25 diluted spinach extracts - fresh and degraded.

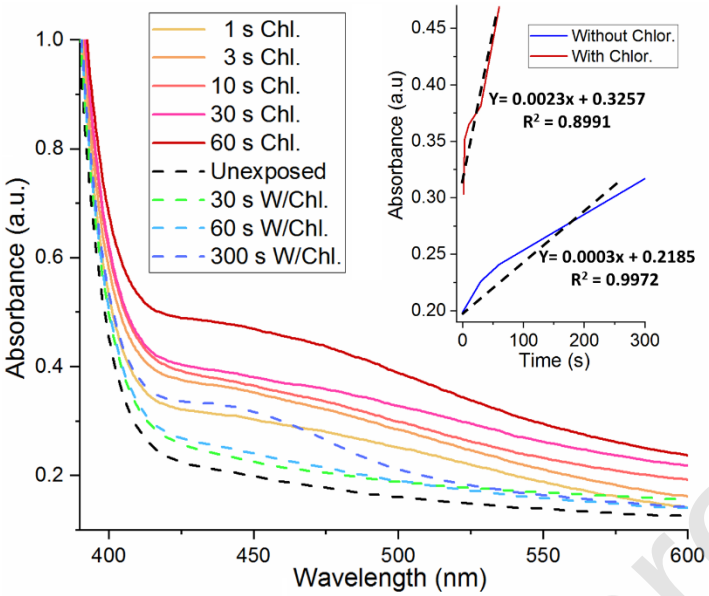


Figure 7 – UV/VIS absorbance of photopatterned samples with spinach extract (Chl) and without (W/Chl.) exposed at different times. The insert is the absorbance measured at 450 nm.

Table 1 – Polyimide-based substrates after photoreduction.

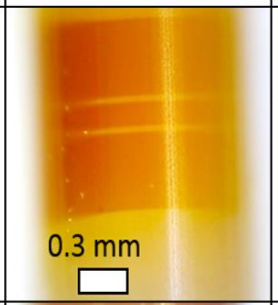
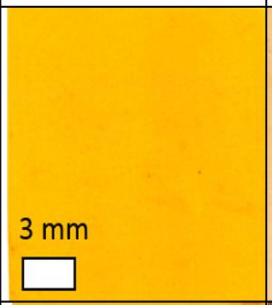
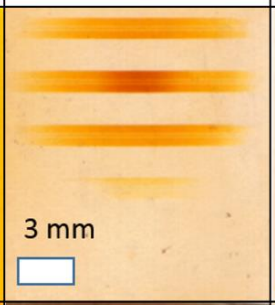
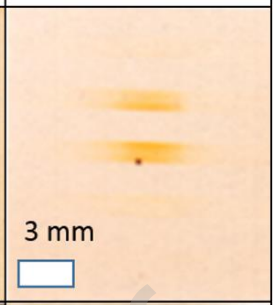
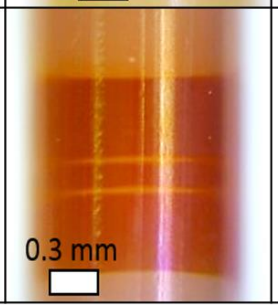
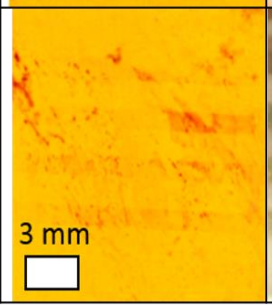
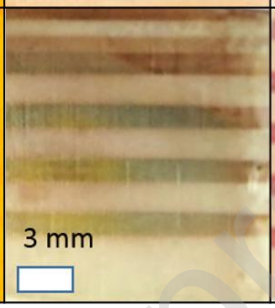
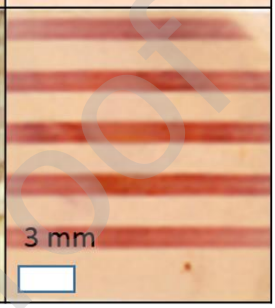
	PEI ULTEM 9085 10 min LED	Polyimide 10 min LED	PEI ULTEM 1000B 10 min LED	PEI ULTEM 1000B 30 sec LED
Without spinach extract				
With spinach extract				

Table 2 - PEI ULTEM 1000B after Ag photoreduction with different sensitiser solutions and for different optical exposure durations.